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Communication

Thermal Conversion of Municipal Biowaste Anaerobic Digestate to Valuable Char

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Abstract: The municipal biowaste anaerobic digestate of a typical waste treatment plant is pyrolyzed under a mild condition (i.e., 540 °C) to directly yield N-doped biochar without performing any subsequent functionalization process. The results confirmed the integration of nitrogen heteroatoms within the carbonaceous framework. The morphological characterization, instead, evidenced the formation of a rather dense biochar with a very low surface area.

Keywords: biochar; biomass; carbon materials; pyrolysis; waste management

1. Introduction

The continuous need for alternative materials to replace fossil sources is rapidly emerging as a promising research field that will catalyze the technological development in the future [1–3]. Interestingly, in the last few decades, the use of carbon has remarkably grown and attracted attention worldwide thanks to the technological push that started with the discovery of its new allotropes (e.g., graphene, graphene oxide, and single- and multi-walled carbon nanotubes) as well as the positive integration of carbonaceous materials into breakthrough and challenging technological fields [4].

However, the production of carbon from natural sources following a simple thermal conversion of biomass from dedicated crops is a technological solution that no longer convinces scientists. It conflicts with food needs, raising concern about the exploitation of cultivation land for non-food purposes. This does not apply to the valorization of municipal biowaste (MBW) as a C feedstock. Indeed, research in this direction is welcome to solve the environmental problems connected with the increasing amount of urban wastes [5,6].

In this context, water-soluble bio-based substances (SBO) have been obtained by the low-temperature alkaline hydrolysis of fermented MBW [2]. These substances have been shown to be efficient and active principles for the formulation and fabrication of products for use in chemistry, agriculture, and animal husbandry. These results offer the possibility to develop a biorefinery that, by integrating biochemical and chemical technology, produces a range of value-added products using MBW as a feedstock. To contribute to the realization of this scenario, the present work reports the pyrolysis of the SBO obtained from the MBW anaerobic digestate of a typical waste treatment plant.

The authors of this work have already carried out previous studies [7–9] on the pyrolysis of several types of biowaste from both animal and vegetal sources. The pyrolysis of the MBW anaerobic digestate has not been reported yet. The present work shows that the pyrolysis of this material, performed under relatively mild conditions (below 700 °C), yields biochar. It points out that, along with other chemical technologies [2,10,11], pyrolysis may be complementary to convert an MBW treatment plant into a biorefinery that produces valued-added products.

2. Materials and Methods

2.1. Reagents and Chemicals

The MBW anaerobic digestate was sourced from the waste treatment plant of the ACEA Pinerolese Industriale S.p.A. (Pinerolo, Italy) by sampling from the biogas production plant line, which is fed with the organic humid fraction derived from the separate collection of urban refuse [11,12]. The MBW was hydrolyzed according to the previous work [10] to obtain the SBO. This material was washed repeatedly with hydrofluoric acid (HF, CAS 7664-39-3, 48%, Merck, Kenilworth, NJ, USA) until the insoluble residue was ash free, then dried in an oven (Mettler, Schwabach, Germany) at 100 °C for one night and maintained in the dark in a closed vial until used. Hereafter, the HF-treated SBO is referred to with the MWDF acronym. The other reagents were: NaOH (CAS 1310-73-2, 98%, Sigma-Aldrich, St. Louis, MO, USA), HCl (CAS 7647-01-0, 37%, Fluka, St. Louis, MO, USA), and KCl (CAS 7447-40-7, 99%, Fluka, St. Louis, MO, USA). All chemicals were used without further purification.

2.2. Pyrolysis Process

The pyrolysis of MWDF (ca. 2 g) was performed in a quartz tube reactor (LTF 12/38/500, Lenton, Hope Valley, UK) under an inert atmosphere (gas: N₂, flux: 250 mL min^{−1}) with the following thermal program: ramp from room temperature (RT) to the target temperature (540 °C, rate: 10 °C min^{−1}), followed by an isothermal step for 1 h, and a non-controlled temperature decrease. The obtained MWDF char was washed twice with deionized water to remove all soluble residues, and then heated overnight at 80 °C in an oven.

2.3. Characterization Methods

A TGA analysis was performed in a TGA Q600 (TA Instruments, New Castle, DE, USA), in nitrogen flux (100 mL min^{−1}). Samples (ca. 10 mg) were heated from RT to 800 °C (heating ramp: 10 °C min^{−1}).

SEM measurements were performed by using a ZEISS EVO 50 XVP microscope (Zeiss, Jena, Germany) equipped with an LaB₆ source and a secondary electron detector, after sputtering a 15 nm Au layer onto the surface.

An elemental analysis of the precursor and the char was carried out in a Thermo FlashEA 1112 CHNS-O analyzer (Thermo Scientific, Waltham, MA, USA). The average values of three replicas are provided for each measurement.

FTIR spectra were recorded in transmission mode in a Vector 22 spectrometer (Bruker, Billerica, MA, USA) equipped with a Global source and a DTGS detector and working with 128 scans at 4 cm^{−1} of resolution in the 4000–500 cm^{−1} range. The FTIR analysis was carried out on sample dispersed in KBr pellets (ratio 1:20).

XRD patterns were obtained on powders by means of a PW3040/60 X'Pert PRO MPD diffractometer (PANalytical, Malvern, UK) equipped with a Cu anode (45 kV, 40 mA) and working in a Bragg–Brentano geometry.

The BET specific surface area (SSA) of MWDF char was quantified by performing a Kr adsorption isotherm at 77 K in an ASAP 2020 instrument (Micromeritics, Norcross, GA, USA). In order to remove the contaminants from the char surface, the sample was outgassed before analysis by heating at 150 °C for several hours under vacuum ($p = 10^{-2}$ mbar).

The ζ potential analysis was performed by dispersing a fixed amount of char (ca. 10 mg) in a 0.01 M KCl saline solution for 1 day and maintaining a constant temperature (25 °C) and pH (6). For the pH correction, HCl and/or NaOH aqueous solutions were added drop-wise. Measurements were carried out using electrophoretic light scattering (ELS) (Zetasizer Nano-ZS, Malvern Panalytical, Malvern, UK) using the Smoluchowski equation, an equilibration time before analysis of 120 s, and five replicas for each specimen. The average values of two replicas were provided [13].

3. Results and Discussion

Figure 1 reports the thermal degradation profiles of MWDF performed under a nitrogen atmosphere. As shown in the figure, the thermo-gravimetric (TG) profile of MWDF presents two main weight losses. The first one is due to the loss of moisture at temperatures below 100 °C (ca. 5 wt.%). The second thermal phenomenon started at the onset temperature of ca. 328 °C and continued up to ca. 550 °C. The analysis of the derivative TG plot (DTG) evidenced that such a degradation phenomenon seems to be bimodal, and probably this is due to an initial weight loss due to the carbohydrate residue of the MWDF, followed by the degradation of the humic-like fraction at higher temperature values (ca. 430 °C), in accordance with the literature [14,15]. A second lower-weight loss of residual organic matter occurs above 550 °C. The results are consistent with previous TGA data for polysaccharides, such as chitosan [16] and humic-like substances isolated from composted biowaste [17]. Since a plateau of stability (in the range 500–600 °C) was registered soon after the main degradation phenomenon, the temperature selected for the pyrolysis treatment was 540 °C.

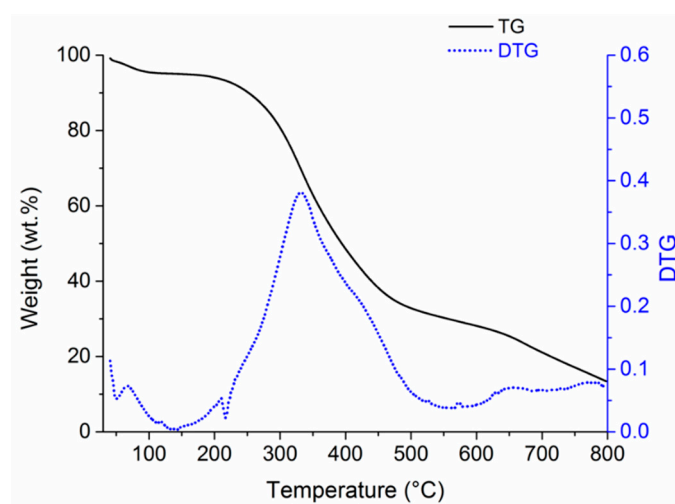


Figure 1. Thermo-gravimetric TG (black solid) and its derivative DTG (blue dotted) analyses of hydrofluoric-acid-treated, bio-based substances (MWDF) heated under a nitrogen atmosphere.

The chemical composition of MWDF and MWDF char were evaluated by an elemental analysis, and the data are summarized in Table 1. As expected, with respect to the pristine MWDF, pyrolysis leads to a significant increase in the %C (from 54.5% to 72.7%) and a drastic reduction of the %H (from 6.2% to 2.2%), thus confirming the carbonization reaction. The heteroatom content (%N), as already evidenced in our previous study [7], remains almost constant during the thermal process (from 7.5% to 7.2%). This phenomenon could be attributed to a progressive inclusion of nitrogen species into cycloaliphatic and/or aromatic structures, forming a N-containing char. Additionally, the HF pretreatment of the precursor consists in a demineralization process, making the ash content in the MWDF almost negligible (below 1 wt.%) [18].

Table 1. The elemental analysis, specific surface area (SSA), and ζ potential measurements.

Samples	%C \pm SD	%H \pm SD	%N \pm SD	C/N	SSA (m ² g ^{−1})	ζ Potential (mV) \pm SD
MWDF	54.5 \pm 0.1	6.2 \pm 0.1	7.5 \pm 0.4	7.3	n.d.	n.d.
MWDF char	72.7 \pm 4.7	2.2 \pm 0.1	7.2 \pm 0.3	10.1	0.51	−45.6 \pm 1.8

To better evaluate the chemical modifications induced by pyrolysis, FTIR spectroscopy has been used to characterize the vibrational behaviors of the two samples (MWDF and MWDF char). As evidenced in Figure 2A, the MWDF spectrum presents characteristic signals at ca. 3400 cm^{−1} due to the O–H and/or N–H stretching modes, a slight shoulder at ca. 3100–3000 cm^{−1} due to the aromatic C–H stretching mode, and a more intense band at 3000–2800 cm^{−1} due to the aliphatic C–H stretching mode, thus suggesting that the aliphatic organic fraction in MWDF is significantly higher than the aromatic one. Additionally, it is possible to observe the presence of bands in the 1700–1500 cm^{−1} range attributable to the presence of carbonyl functionalities, mostly amide (ca. 1650 cm^{−1}) and carboxylate salts (ca. 1520 cm^{−1}) [19]. The char produced by pyrolysis treatment at 540 °C, instead, confirmed the carbonization process of MWDF, with the loss of the polar functionalities and the incipient formation of a broad signal in the 1600–1000 cm^{−1} range due to the presence of C–C and C=C groups [7].

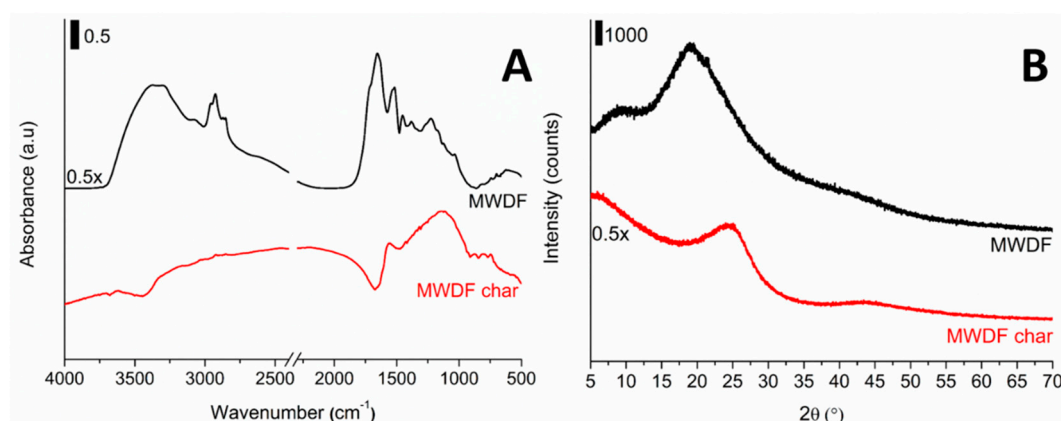


Figure 2. Panel (A) FTIR spectra in the 4000–500 cm^{−1} range of MWDF (black curve) and MWDF char (red curve); Panel (B) XRD patterns of MWDF (black curve) and MWDF char (red curve).

From the structural viewpoint, the XRD patterns of both MWDF and its char confirmed the absence of extended structural organization, showing only a broad signal centered in the ca. $2\theta = 23\text{--}25^\circ$ range with a slight shift toward ca. $2\theta = 26^\circ$ in the case of MWDF char, thus suggesting the formation of graphitic-like structures (Figure 2B).

The SEM micrograph for MWDF char (Figure 3) revealed a rather dense material with a certain degree of surface roughness. Such a dense structure was also confirmed by the very low value of SSA (0.51 m² g^{−1}), which was measured by using Kr as a probe molecule in order to evaluate with accuracy such a low specific surface area [20]. The surface charge of MWDF char was evaluated by performing a ζ potential measurement at constant pH, temperature, and ionic strength, highlighting the formation of strongly negatively charged surfaces (see Table 1) useful for developing interactions with positive substrates. This behavior is in agreement with the literature for analogous systems [7,21].

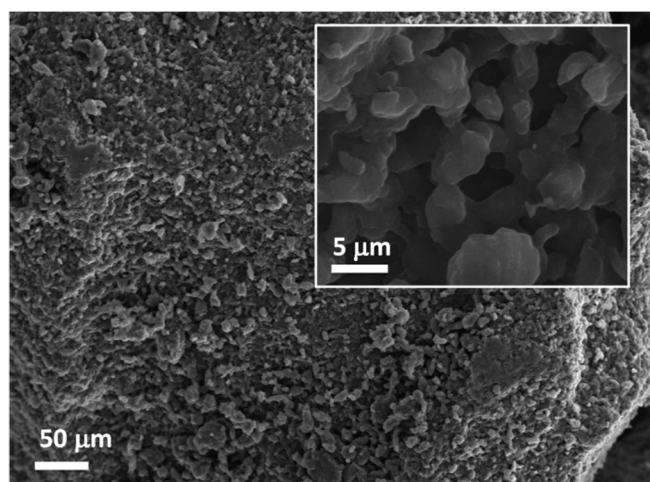


Figure 3. The SEM micrograph of MWDF char at low and high (inset) magnifications.

The research on the sustainable production of chemicals and/or carbon/char is a very promising research field that has continuously caught the attention of experts worldwide [22–27]. Among the possible processes, the direct N-doping of carbon makes these materials very interesting for their exploitation as supercapacitors [28,29] due to the enhanced conductivity, wettability, and electro-catalytic activity induced by the presence of heteroatoms within the carbon network [30]. In this context, the here-described research study proposes biowaste as an alternative precursor for the production of N-doped carbons potentially exploitable in electrochemical applications. The present paper presents a case study showing how municipal biowastes can be valorized for the production of bio-based materials. Relevant benefits are expected for society from promoting research of this scope as the present case study aims to do. These benefits include offering worthwhile scope to the research community to promote further studies, developing technology and bio-based products from biowaste, and reducing biowaste landfilling, thus promoting a new biowaste-based industry.

4. Conclusions

In this study, the MWDF has been converted to biochar. The selected process was pyrolysis under mild thermal conditions (i.e., 540 °C). The choice of maintaining mild conditions of biomass-to-char conversion has allowed us to retain the N content within the product's structure. This makes the above biochar attractive for future applications as a N-containing carbon material. The product's morphological and physicochemical characterization has revealed a rather dense carbonaceous material with very low specific surface area values. This result offers scope for further work that aims to increase the SSA by a proper catalyst or activation procedure. Within its limitations, the reported experimental work points out that is possible to convert MBW into valuable char and that pyrolysis is a valuable technology to consider when integrating other chemical and biochemical technologies for the valorization of biowaste as a source of value-added products.

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